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CHEMICAL OXYGEN CONSUMED AND ITS RELATIONSHIP TO B.O.D.*

The oxidation of organic compounds contained in sewage and polluted water has interested workers in the field of sanitary science for a number of decades. Frankland [1] in 1870 first proposed the fore-runner of our modern Biochemical Oxygen Demand test. He measured the decrease in the dissolved oxygen content of samples of water from the River Thames. However, his conception of the process taking place in such samples is radically different from that of later workers. He believed that it was purely a chemical oxidation by the oxygen dissolved in the water.

In 1884 Dupre [2] showed as a result of his research that the decrease in the dissolved oxygen content of incubated samples was caused by the metabolic activities of the organisms present. Thus, our modern concept of biochemical oxidation arose.

This concept has resulted in many research studies by various investigators during the past half century. Phelps [3] and Theriault [4] were among the first to propose the concept of an unvarying velocity constant "k" of 0.1. This constant has more or less been universally accepted in the fields of stream sanitation and sewage treatment until within the last few years. It was not

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until 1948 when Ruchhoft et al [5,6] and Gotaas [7] showed that although the course of biochemical oxidation followed the unimolecular formula, nevertheless, the velocity constant "k" might vary between the values of 0.07 to 0.25.

This variance of the constant "k" has an important bearing on the correlation of the oxygen demand of polluted waters as determined biochemically to that as determined by strictly chemical means. It is because of this variance in the metabolic rates of the microbic population present that we can expect limited correlation between these two parameters. Another important factor that enters into consideration is the fact that chemical methods cannot distinguish between a biologically stable and unstable organic material. This is well illustrated in the case of the oxidation of cellulosic materials which are present in raw sewage. Cellulose is one of the complex organic compounds that is oxidized quantitatively by chemical means and is not attacked biochemically under aerobic processes usually encountered in stream purification or sewage treatment. On the other hand, there may be present organic acids which form a source of food for bacteria. These organic acids were not attacked by chemical oxidants that are commonly used. Recently it has been shown [8] that acid dichromate in the presence of a silver catalyst will oxidize these organic acids.

In spite of the fact that the oxygen consumed by chemical and biochemical methods does not necessarily agree, numerous attempts have been made to devise chemical methods that would give estimates of the biochemical oxygen requirements in shorter time periods than required biochemically. As pointed out previously, although limited correlation between these two parameters exists in most cases, each has its place in the field of stream sanitation, industrial waste and sewage treatment.

The biochemical oxygen demand determines the quantity of oxygen required for biochemical stabilization when a sewage or industrial waste is discharged into a surface water. This test is made under pH and temperature conditions that simulate the natural conditions present. The oxygen consumed test, on the other hand, is a measure of the chemical oxidant required to oxidize the organic matter under very special and unnatural conditions, i.e., high acidities and temperatures.

In the case of many industrial wastes, there may be present toxic materials which inhibit the normal biochemical processes. Nevertheless, such a waste when discharged to a stream may exert a deleterious effect in various ways and a chemical oxygen consumed test may be used to estimate the concentration of such pollution. Inorganic wastes, such as those containing ferrous iron or sulfite, are best evaluated by means of the oxygen consumed test. This test may be valuable in determining the approximate strength of an unknown industrial waste and

thereby an estimate of the range of dilutions needed for determining the B.O.D. can be ascertained in a minimum time. Since a chemical method for determining oxygen consumed can give us valuable information, it is desirable to review the various procedures that have been proposed.

Oxygen Consumed Methods

For years past the use of permanganate as an oxidizing agent has been accepted by Standard Methods (9). That those procedures using permanganate are not entirely satisfactory is well shown by some of the numerous modifications that have been proposed (10,11,12,13,14,15,16). Because of the variable results obtained with permanganate, other oxidizing agents have been used by various research workers. Of these, only potassium dichromate and iodic acid have been received favorably by sanitary chemists. Recently (8) a comparative study was made in our laboratory of the more promising methods that have been proposed. This study included the dichromate methods proposed by Madison (17), by Ingols and Murray (18), and by Moore, Kroner and Ruchhoft (19). It had been shown by Muers (20) that silver sulfate could be used as an oxidation catalyst in conjunction with a dichromate method. Consequently, the use of silver sulfate was also studied in conjunction with the Moore method (19). The iodic acid method first proposed by Dzyadzio (21) and later modified by Johnson, Tsuchiya and Halvorson (22), and the Standard permanganate method (9) were also studied along with the dichromate methods.

A portion of the results of this study carried out with four typical industrial wastes and four organic compounds are summarized in Table 1. From the statistical comparison of the various methods, as given in Table 1, and from other considerations, both the Standard permanganate and the Madison procedures were eliminated as being unsatisfactory.

The data given in the last column of Table 1 are a measure of the precision of the various methods. For example, on the organic dye waste, it is shown that in 95 per cent of the cases a single determination with the iodate method will come within 11.5 per cent of the mean value. With the Moore method on this same waste, results can be expected such that 95 per cent of the time a single determination will come within 3 per cent of the mean. Both the Standard permanganate and Madison's methods are shown to be inferior to the other methods. On all subsequent samples both the Ingols and Moore procedures gave the best reproducibility, even though the former was slightly inferior to the iodate method on the organic dye waste.

When silver sulfate is used as a catalyst in conjunction with the regular Moore method the usefulness of the latter is extended in many cases. This is particularly true when a given waste contains aliphatic acids or alcohols. Such acids are not oxidized by the regular procedure but are quantitatively broken down when silver sulfate is used as a catalyst.

There are other factors involved in the selection of a method for the determination of oxygen consumed besides the precision involved. For example, the time involved in running five samples and five blanks with the iodic acid method is seven and three-fourths hours. Of this time, seven hours are actually spent in manipulation. The same holds true for Madison's procedure. With both Madison's and Ingols' methods, the endpoints on the titration are hard to judge which is one of the factors causing poor reproducibility. In addition, with these two methods the sample size that can be used is limited, which introduces additional errors, especially when strong wastes are being studied.

Although the permanganate method requires less manipulation time than any of the other methods, it is quite difficult to obtain uniform results. Some of the replicates may boil more vigorously than others, thereby concentrating the solution which will affect the results. The effect of agitation on the sample is also noticeable as manganese dioxide tends to precipitate and if the sample is not agitated frequently, variable results will be obtained. In many cases the precipitated manganese dioxide is difficult to dissolve. Sample size is also important for if more or less than 50 per cent of permanganate is used variable results are obtained.

The Moore method is intermediate as far as time and manipulation are concerned. With this method, sample size is not as critical and the endpoint is quite sharp and reversible. The use of silver sulfate as a catalyst, previously mentioned, extends the usefulness of this

method. Aliphatic acids and alcohols are oxidized quantitatively as in the case of biological oxidation. This fact is well illustrated in the results shown in Table 2.

Uses of Oxygen Consumed in Conjunction with B.O.D.

Sewage

In recent years many investigators have attempted to substitute oxygen consumed procedures for the Standard B.O.D. test. However, as pointed out previously, this substitution is not justified in most cases as these methods are two distinct parameters and must be considered as such.

Among the first workers to attempt a comparison between oxygen consumed and B.O.D. on sewage were Mohlman and Edwards [23] in 1931. Although the method used by these investigators, as well as that used by Burtle and Buswell [24], gave precise results, they were unable to correlate satisfactorily these two parameters.

Rhame [25], using an oxygen consumed method, later modified by both Madison [17] and Ingols [18], also attempted such a correlation. From his results he concluded that it was difficult to obtain reliable results but thought that the difficulty lay in the oxygen consumed technique used. In a later study [26], he found that the results obtained with raw and settled sewage were radically different. In the case of the raw sewage the results were much more erratic than in settled sewage. However, in Rhame's determination of oxygen consumed he used an acid concentration much less than 50 per cent by volume. These factors of acid concentration and character of sewage will be discussed later.

Ingols also attempted to correlate oxygen consumed with B.O.D. and in his study he used raw and settled sewage as well as trickling filter effluent. He multiplied his oxygen consumed values by 0.68 which assumes a velocity constant of 0.1. Even after such adjustment of the data, the oxygen consumed values obtained were still higher than the corresponding B.O.D. This is particularly true of the filter effluent as might be expected. This higher O.C./B.O.D. ratio is due to the fact that the organic compounds remaining and those formed during biochemical oxidation are stable biochemically but are still subject to chemical oxidation by a strong oxidant.

In Table 3 are given some comparative data on oxygen consumed and the biochemical oxygen demand of domestic sewage containing no industrial waste of any kind. In connection with these data, two factors should be kept in mind. First, all sewage samples were filtered through cotton, thus removing any gross particles (including cellulosic material) present in the original sample. Secondly, the oxygen consumed of the sample was determined using 33 per cent by volume of sulfuric acid. These two factors have an important bearing on the oxygen consumed values obtained by the dichromate method and merit closer consideration.

As mentioned previously, cellulosic materials present in a sewage or industrial waste are oxidized quantitatively by chemical oxidants. They are not oxidized biochemically under aerobic

conditions. By the removal, therefore, of such materials from a given substrate such as domestic sewage one would expect a somewhat closer correlation between the oxygen consumed and B.O.D. values obtained. This has been found to be true by other investigators already mentioned and is borne out by the data presented in Table 3.

The second factor mentioned above, namely the effect of acid concentration on the oxygen consumed value obtained has also been studied before [19]. The lower the acid concentration in the reflux mixture, the lower the oxygen consumed will be. This factor no doubt has a bearing on the results as shown in this table.

It would be extremely difficult to set up the exact conditions in the oxygen consumed test that would duplicate B.O.D. values. Such duplication might be obtained in a given short series of samples but as a rule the variables are such that constancy of the O.C./B.O.D. ratios cannot be expected in sewage samples.

Polluted Streams

A small stream (Lytle Creek) under study at the Environmental Health Center receives the effluent from a primary sewage treatment plant. This effluent comprises approximately 75 per cent of the stream flow. In Table 4 the ratio of the oxygen consumed to the 5-day B.O.D. is given. If we consider the first point (Station 6) which is above the sewage effluent outfall, we note that biologically the stream is stable but contains organic compounds which are chemically oxidized. The effect of removing the gross particles by

primary sedimentation is seen in the data for the sewage effluent. Here the ratio between the oxygen consumed and B.O.D. values is smaller. As one progresses down the stream a change in the O.C./B.O.D. ratio is seen. This again is simply an increase in the biologically stable material which is readily oxidized chemically.

Another factor that is noticeable from the data presented in Table 4 is the variation in the O.C./B.O.D. ratio for the same Station at various periods of the year. The data show that it would be impossible to predict (even though the stream is receiving the same type of sewage throughout the year) what the B.O.D. would be at a given point from the results of one survey when the oxygen consumed alone is determined.

In Table 5 a comparison between the O.C./B.O.D. ratio is given on a river receiving the wastes from an oil refinery. These data again show that above the point of discharge the stream water has a high O.C./B.O.D. ratio which indicates again that although biological stability and a low B.O.D. has been obtained the river contains considerable material capable of oxidation by chemical methods. It is also apparent that a large portion of the discharged effluent from the oil refinery is amenable to biological oxidation, since the oxygen consumed to 5-day B.O.D. ratio is much smaller.

One of the difficulties encountered in applying oxygen consumed methods to polluted streams is the relatively small amount of oxidizing agent required to oxidize the organic material present. If, for

example, one uses the same normality of dichromate in stream pollution surveys as is used for sewage or industrial wastes, the consumption of the oxidizing solution is small which necessarily entails a large back titration. If, on the other hand, a weaker oxidizing solution is used the maximum amount of organic material will not be oxidized. It is necessary, therefore, in each investigation to determine whether the maximum oxygen consumed or the maximum accuracy is desired. For example, when 0.025 N dichromate is used as the oxidizing agent the values obtained are about 10 per cent lower than with the 0.2500 N reagent. The ferroin indicator is also less sensitive at this lower dichromate concentration. As a rule the application of oxygen consumed methods to the study of polluted streams has been limited. Lawrence [27,28] used the Standard permanganate test in his study of the pollution of the Androscoggin River to determine the rate of application of sodium nitrate to prevent septicity.

Industrial Wastes

Perhaps the widest use of oxygen consumed methods in the future will be in the field of industrial waste analyses. This is easily understandable since such determinations require a relatively short time and as mentioned before many wastes contain materials which are toxic to the microflora and fauna responsible for biochemical action. This last factor is one of the major causes of the wide range in B.O.D. results obtained with various dilutions of toxic wastes. This

is aptly illustrated by the range of B.O.D. values shown for the textile dye wastes and the oil refinery waste as given in Table 6.

There are, however, many industrial wastes in which oxygen consumed methods can give valuable information. For example, if a given waste is fairly consistent in composition, then a mean ratio between the oxygen consumed and B.O.D. may be determined. Once such a ratio is determined much time will be saved in the operation of a pilot plant to determine the best method for treatment of the particular waste. Whether or not the oxygen consumed test can be used to control the ultimate treatment process can only be determined after additional experimentation.

In Table 6 are given the comparisons between oxygen consumed and 5-day B.O.D. of a few industrial wastes and on a sample containing one of the common synthetic detergents. In the case of the first three wastes a ratio between these two parameters should be fairly easy to determine. However, with the last two wastes variable B.O.D. results are obtained (depending upon the dilution used) and such wastes would require extensive tests to determine the most probable ratio, and to use oxygen consumed methods as control measures.

Conslusions

(1) The use of silver sulfate as a catalyst greatly extends the completeness of the oxidation by the acid dichromate procedure when the use of silver is compatible with the waste.

(2) Oxygen consumed methods and the B.O.D. test are two distinctly different parameters which indicate biological and chemical oxygen requirements which have no a priori intrinsic relationship.

(3) In those wastes containing materials toxic to biological action, or if the approximate chemical oxidizability of a given waste is desired, an oxygen consumed method can be used advantageously.

(4) In domestic sewage from which the settleable solids have been removed, a satisfactory correlation can be obtained between the oxygen consumed and 5-day B.O.D.

(5) In streams receiving domestic sewage the O.C./B.O.D. ratio increases as the stream becomes increasingly biologically stable. This is due to the presence of microflora and fauna which contain organic compounds that are oxidized by chemical methods and are biologically stable.

(6) Where a given industrial waste is fairly constant in composition and contains no toxic materials, a satisfactory O.C./B.O.D. ratio may be determined. In such cases, the oxygen consumed test, with occasional checks against B.O.D., may be used for control purposes in the treatment of the particular waste.

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TABLE 1

Statistical Comparison of Oxygen Consumed Methods

Compounds or Waste and Method Used	Mean	Standard Deviation	100 C.L./$\bar{x}$ (1)
Organic Dye Waste			
Iodate	960	39.4	11.5
Ingols	1153	73.6	14.4
Madison	690	211	67.5
Permanganate	463	33.3	16.2
Moore	1183	15.9	3.0
Ortho-cresol			
Iodate	575	14.0	6.8
Ingols	543	12.9	5.3
Madison	459	30.5	15.0
Permanganate	443	22.8	11.7
Moore	530	5.1	2.3
Oil Refinery Caustic Waste			
Iodate	50900	2274	12.4
Ingols	46000	874	4.3
Madison	32200	2838	19.9
Permanganate	29100	1232	9.6
Moore	48400	347	1.6
Moore-Ag_2SO_4	57500	742	2.9
Textile Dye Waste			
Iodate	27500	1634	16.5
Ingols	35200	569	3.7
Moore	36600	204	1.3
Moore-Ag_2SO_4	-	-	-
Glycocoll			
Iodate	-	-	-
Ingols	417	18.3	10.0
Moore	592	4.5	1.7
Moore-Ag_2SO_4	607	4.5	1.7
Distillery Waste			
Ingols	356	14.8	9.3
Moore	344	6.0	4.0
Moore-Ag_2SO_4	902	5.3	1.3

(1) A single determination will come within the stated percentage of the true mean 95 per cent of the time.

TABLE 2

Effect of Silver Sulfate on Moore Oxygen Consumed Method

Compound (1)	Mean O. C. p.p.m.		Range of O.C. p.p.m.		Per cent of Theory	
	Regular	With Ag_2SO_4	Regular	With Ag_2SO_4	Regular	With Ag_2SO_4
Acetic Acid	26	1014	38	62	2.4	95.1
Alanine	326	870	25	17	33.5	80.6
Furoic Acid	1074	1254	57	14	83.6	97.6
o-cresol	2095	2413	54	43	83.2	95.8
Ethanol (2)	619	1672	67	33	29.7	80.1
Benzene	240	250	18	28	7.8	8.1
Pyridine	34	20	6	17	1.3	0.8

(1) Ten replicates of each compound with and without the silver catalyst were run.

(2) Eighty-seven per cent C_2H_5OH.

TABLE 3

Relation Between Oxygen Consumed[1] and 5-Day B.O.D. of Domestic Sewage[2]

Sample	Oxygen Consumed	5-Day B.O.D.	O.C./B.O.D.
1	187	200	0.94
2	347	340	1.02
3	329	338	0.97
4	162	156	1.04
5	263	261	1.01
6	294	301	0.98
7	230	241	0.95
8	205	145	1.41
9	151	149	1.01

(1) Thirty-three per cent by volume of H_2SO_4 used in conjunction with the Moore method.

(2) Sewage was filtered through cotton.

TABLE 4

Relation Between Oxygen Consumed and the 5-Day B.O.D.

on Stream Samples

Oxygen Consumed/B.O.D.

Date	STATION (MILES FROM MOUTH)							
	Above Effluent	Sewage Effluent	Below Effluent					
	6.0		5.8	5.1	4.0	3.0	2.2	0.3
12/6/49	8.6	1.8	2.2	1.6	2.7	3.1	5.0	5.5
3/14/50	6.5	3.3	3.3	-	-	-	4.0	4.6
8/16/50	9.1	1.5	1.6	1.9	5.3	8.2	-	-
9/29/50	20.2	1.6	1.3	1.8	4.1	-	8.7	8.2

TABLE 5

Relation Between Oxygen Consumed and 5-Day B.O.D.

on Stream Polluted by Oil Refinery Waste

Station	Oxygen Consumed/ 5-Day B.O.D.
Above Plant Effluent	7.8
Just Below Plant Effluent	2.0
1,000 Yards Below Plant Effluent	1.9

TABLE 6

Oxygen Consumed to B.O.D. Ratio of Industrial Wastes

Waste	5-Day B.O.D.	Oxygen Consumed		Ratio O.C./B.O.D. Regular Method	
		Regular Method	Regular Plus Ag_2SO_4	Maximum	Minimum
Dye Waste	450	1,180	-	2.62	-
Distillery Waste	725	344	902	.47	-
Sodium Lauryl Sulfate	1,300	1,530	1,800	1.18	-
Soap Manufacturing Waste	303	530	-	1.74	-
Textile Dye Waste	280-2,000	37,600	-	134	18.8
Oil Refinery Waste	8000-63000	48,400	57,500	6.1	.77